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"AN IMPROVED ELECTROLYTIC PROCESS AND CELL FOR THE PRODUCTION OF m-TOLUIDINE FROM m-NITROTOLUENE"

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-110001, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

The following specification describes the nature of this invention.

PRICE : TWO RUPEES

151037

This is an invention by Handady Venkatakrishna Udupa, Director; Payyallur Narayanan Anantharaman, Scientist and Michael Noel, Junior Scientific Assistant all of Central Electrochemical Research Institute, Karaikudi 623 006, India- all Indian citizens.

This invention relates to the improvements in or relating to the electrolytic reduction of m-nitrotoluene (mNT) to m-toluidine (m-T)

Hitherto it has been proposed to reduce mNT by Bechamp reduction using iron and hydrochloric acid. Electro reduction of mNT is also reported in acid medium using copper cathode. With relating cathodes current efficiency(C.E.) upto 84.0% is reported at a current density(C.D) of 5A/dm^2.

These methods are open to the following objections. In the Bechamp method use of metal powder is involved and disposal of large quantity of Fe-sludge remains a problem. In the electrochemical method as mNT to catholyte volume ratio increases the current efficiency is lowered and hence sufficient quantity of mNT cannot be reduced by this method to recover the m as its solid sulphate from the catholyte. Hence the catholyte cannot be reused in this method.

The object of this invention is to obviate these disadvantages by reducing mNT electrochemically using an addition agent which allows the reduction at higher density with high current efficiency. 30 to 35 gms of mNT is reduced per 100 ml of catholyte. The m-T formed is converted to it's salt and at higher concentrations and lower temperatures it separates out as a solid. This allows the economic recovery of m-T and reuse of catholyte. With this addition agent, with stationary cathode a current density of 5-10 A/dm^2 and with a rotating cathode a current density of 15-25 A/dm^2 is applied with a current efficiency of 70%

To these ends the invention broadly consists in reducing a suspension of mNT in 30-40% H_2SO_4 containing 2-3% titanic sulphate and 0.05 - 0.2% copper sulphate as the catholyte. 30-40% H_2SO_4 is used as the anolyte, a lead strip or lead silver alloy is used as the anode, a ceramic pot is used as the diaphragm and copper in the form of a vessel or sheet serves as the cathode for stationary electrode conditions. For rotating electrode

conditions a cylindrical Cu rod is used. The electro reduction is carried out in a closed vessel with provisions for stirrer, thermometer, porous pot and condenser. A cathode current density ranging from 5 to 10 A/dm^2 for stationary cathode and 15-25 A/dm^2 for rotating cathode is applied. mNT is added in small quantities at regular intervals. The temperature during electrolysis is maintained between 40-60°C. 10% excess of the charge required to reduce the mNT completely is passed. The m-T formed is then estimated by bromination method. Yield upto 97% and current efficiency upto 86.1% is obtained (Example 1).

When the electrolysis is carried out adding mNT in smaller instalments till 25-35 gms of mNT per 100 ml of catholyte is reduced, mT formed separates out as m-toluidine sulphate (mTS). The catholyte is cooled to 20-35°C and filtered. The H_2SO_4 content of the catholyte is made up to 35% by addition of fresh H_2SO_4 and reused for reducing more mNT. 13-17 gms of mNT per 100 ml of catholyte may be reduced at each reuse. Example 2 gives the details of the reuse of catholyte three times. However the catholyte may be reused ten times in the same way.

mT may be recovered from mTS by dissolving it in water neutralising with liquor ammonia. The free base liberated is steam distilled to get pure m-T. With 98% LR grade mNT used during the electrolysis the mT obtained by this method is 99% pure. The recovery efficiency from mTS to mT is found to be between 80-85%

The following are the main advantages of the process:

1) In comparison with the chemical method use of metal powder and the difficulty of dealing with Fe sludge is completely avoided. This is the advantage over the chemical method.

2) Use of addition agents enables use of stationary cathodes and higher current densities. These factors respectively enables the use of simpler and smaller cell design.

3) The recovery of mT as mTS and reuse of catholyte many times enabling lower cost of production to be achieved.

4) Isolation of the product is very simple and the isolated product is 99% purity.

EXAMPLE 1

Cell	:	1000 ml glass beaker
Cathode	:	Rotating cylindrical copper rod
Cathode area	:	66 cm^2
Cathode c.d.	:	15 A/dm^2
Anode	:	Lead
Anode area	:	0.9 dm^2
Catholyte	:	500 ml of 35% H_2SO_4 containing 2.4% $Ti(SO_4)_2$ and 0.1% $CuSO_4.5H_2O$
Anolyte	:	100 ml 35% H_2SO_4
Average cell voltage	:	6.4V
Temperature	:	45-50°C
Total charge passed	:	145 A hrs
Total weight of mNT reduced	:	115 gms
Temperature of to which the catholyte was cooled	:	20°C
Total weight of solid mTS separated out	:	9.8 gms
Total mT formed	:	67.25 gms
Yield	:	74.87%
Current efficiency	:	89.82%
Energy consumption	:	13.74 Kwh/kg mT produced

EXAMPLE 2

Conditions:

Cell	:	1000 ml glass beaker
Cathode	:	Copper plate
Cathode area	:	1.9 dm^2

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Cathode c.d.	:	8 A/dm^2
Anode	:	Lead
Anode area	:	6.9 dm^2
Catholyte	:	500 ml of 35% H_2SO_4 containing 2.4% $Ti(SO_4)_2$ and 0.1% $CrSO_4.5H_2O$
Anolyte	:	100 ml of 35% H_2SO_4
Average cell voltage	:	5.0V
Temperature	:	45-50°C
<u>First batch:</u>		
Amount of mNT ADDED	:	173.3 gms
No. of amp hrs passed	:	270 A hrs
Temperature to which catholyte was cooled	:	20°C
Weight of mTS isolated	:	118.8 gms
<u>Rouge 1</u>		
Amount of mNT added	:	89.4 gms
No. of amp hrs passed	:	97.5 A hrs
Temperature to which catholyte was cooled	:	32°C
Weight of mTS isolated	:	78.4 gms
<u>Rouge 2</u>		
Amount of mNT added	:	81.0 gms
No. of amp hrs passed	:	112.5 amp hrs
Temperature to which catholyte was cooled	:	20°C
Weight of mTS isolated	:	60.3 gms
<u>Rouge 3</u>		
Amount of mNT added	:	81.0 gms
No. of amp hrs passed	:	112.5 A hrs
Temperature to which catholyte was cooled	:	28°C
Weight of mTS isolated	:	118.0 g.

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Overall

Total weight of mNT reduced	:	404.7 gms
Total weight of mT estimated as solid	:	244.9 gms
Total weight of mT in solution	:	36.4 gms
Overall yield efficiency	:	89.1%
Overall current efficiency	:	71.3%
Energy consumption	:	11.6 kwh/kg mT produced

Dated This 22nd day of January, 1979

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THE PATENTS ACT. 1970

COMPLETE SPECIFICATION

(Section—10)

" AN IMPROVED ELECTROLYTIC PROCESS AND CELL FOR THE PRODUCTION OF m-TOLUIDINE FROM m-NITROTOLUENE."

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi - 110001, India, an Indian registered body incorporated under the Registration of Societies act (Act XXI of 1860).

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

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This is an invention by Handady Venkatakrishna Udupa, Director; Payyallur Narayanan Anantharaman, Scientist and Michael Noel, Junior Scientific Assistant, all of Central Electrochemical Research Institute, Karaikudi-623 006, all Indian citizens.

This invention relates to an improved electrolytic process and cell for the production of m-toluidine from m-nitrotoluene.

Hitherto it has been proposed to reduce m-nitrotoluene by Bechamp reduction using iron and hydrochloric acid. Electro-reduction of m-nitro toluene is also reported in acid medium using copper cathodes. With rotating cathodes, current efficiency upto 84.0% is reported at a current density of 5 A/dm^2. At higher current densities, the current efficiency is much lower.

These methods are open to the following objections. In the Bechamp method use of metal powder is involved and dispersal of large quantity of Fe-sludge remains a problem. In the electrochemical method as m-nitro toluene to catholyte volume ratio increases the current efficiency is lowered and hence sufficient quantity of m-nitro toluene cannot be reduced by this method to recover the m-toluidine as its solid sulphate from the catholyte. Hence the catholyte cannot be reused in this method.

The object of this invention is to obviate these disadvantages by reducing m-nitro toluene electrochemically using an addition agent which allows the reduction at

higher current density with high current efficiency. 30 to 35 g of m-nitro toluene is reduced per 100 ml of catholyte. The m-toluidine formed is converted to its salt and at higher concentrations and lower temperatures it separates out as a solid. This allows the economic recovery of m-toluidine and reuse of catholyte. With this addition agent, with stationary cathode a current density of 5-10 A/dm^2 and with a rotating cathode a current density of 15-25 A/dm^2 is applied with a current efficiency of 70%.

The other main objectives of the process are to achieve:

1) in comparison with the chemical method to avoid use of metal powder and the difficulty in dealing with Fe sludge;

2) Use of addition agents to enable use of stationary cathodes and higher current densities. These factors respectively enables the use of simpler and smaller cell design; and

3) the recovery of m-toluidine as m-toluidine sulphate and to reuse of catholyte many times to enable lower cost of production to be achieved.

Accordingly this invention provides an improved electrolytic process for the production of m-toluidine from m-nitro toluene in an acid medium as an electrolyte that is characterised in that m-nitro toluene is electrochemically

reduced as a suspension in an electrolyte consisting of sulphuric acid and an ~~ammix~~ admixture of 2-4% of titanic sulphate and 0.05 - 0.2% of hydrated copper sulphate as an additive, cooling and isolating the m-toluidine sulphate formed and reusing the electrolyte for further reduction.

To these ends the invention broadly consists in reducing a suspension of m-nitro toluene in 30-40% H_2SO_4 containing 2-3% titanic sulphate and 0.05-0.2% copper sulphate as the catholyte. 30-40% H_2SO_4 is used as the anolyte, a lead strip or lead silver alloy is used as the anode, a ceramic pot is used as the diaphragm and copper in the form of a vessel or sheet serves as the cathode for stationary electrode conditions. For rotating electrode conditions a cylindrical copper rod is used. The electro-reduction is carried out in a closed vessel with provisions for stirrer, thermometer, porous pot and condenser. A cathode current density ranging from 5 to 10 A/dm^2 for stationary cathode and 15-25 A/dm^2 for rotating cathode is applied. m-Nitro toluene is added in small quantities at regular intervals. The temperature during electrolysis is maintained between 40-60°C. 10% excess of the charge required to reduce the m-nitro toluene completely is passed. The m-toluidine formed is then estimated by bromination method. Yield upto 97% and current efficiency upto 86.1% is obtained (Example 1)

When the electrolysis is carried out adding m-nitro toluene in similar instalments till 25-35 g of m-nitro

toluene per 100 ml of catholyte is reduced, m-toluidine formed separates out as m-toluidine sulphate. The catholyte is cooled to 20-35°C and filtered. The H_2SO_4 content of the catholyte is made up to 35% by addition of fresh H_2SO_4 and reused for reducing more m-nitro toluene. 13-17 g of m-nitro toluene per 100 ml of catholyte may be reduced at each reuse. Example 2 gives the details of the reuse of the catholyte three times. However, the catholyte may be reused ten times in the same way.

m-Toluidine may be recovered from m-toluidine sulphate by dissolving it in water neutralising with liquor ammonia. The free base liberated is steam distilled to get pure m-toluidine. With 98% LR grade m-nitro toluene used during the electrolysis the m-toluidine obtained by this method is 99% pure. The recovery efficiency from m-toluidine sulphate to m-toluidine is found to be between 80-85%.

The invention is further illusted by following examples.

EXAMPLE 1

Cell:	..	1000 ml Glass beaker
Cathode:	..	Rotating cylindrical copper rod.
Cathode area:	..	66 cm^2
Cathode current density:	..	15 A/dm^2
Anode:	..	Lead
Anode area:	..	90 cm^2

Catholyte:	..	500 ml of 35% H_2SO_4 containing 2.4% $Ti(SO_4)_2$ and 0.1% $CuSO_4.5H_2O$.
Anolyte:	..	100 ml 35% H_2SO_4
Average cell voltage:	..	6.4V
Temperature:	..	45-50°C
Total charge passed:	..	145 amp-hours
Total wt. of m-nitro toluene reduced:	..	115 g
Temperature to which the catholyte was cooled:	..	20°C
Total wt. of solid m-toluidine sulphate separated out:	..	9.8 g
Total m-toluidine formed:	..	67.25 g.
Yield:	..	74.87%
Current efficiency:	..	69.82%
Energy consumption:	..	13.74 Kwh/kg m-toluidine produced.

EXAMPLE 2

Cell:	..	1000 ml Glass beaker
Cathode:	..	Copper plate
Cathode area:	..	1.9 dm^2
Cathode current density:	..	8 A/dm^2
Anode:	..	Lead
Anode area:	..	0.9 dm^2
Catholyte:	..	500 ml of 35% H_2SO_4 containing 2.4 $Ti(SO_4)_2$ and 0.1% $CuSO_4.5H_2O$
Anolyte:	..	100 ml of 35% H_2SO_4
Average cell voltage:	..	5.0V
Temperature:	..	45-50°C

First batch:

Amt. of m-nitro toluene added:	.. 173.3 g
No. of amp-hrs passed:	.. 270 A-hrs
Temperature to which catholyte was cooled:	.. 20°C
Wt. of m-toluidine sulphate isolated:	.. 118.0 g

Reuse 1

Amt. of m-nitro toluene added:	.. 69.4 g
No. of amp-hrs passed	.. 97.5 amp-hrs
Temperature to which catholyte was cooled:	.. 32°C
Wt. of m-toluidine sulphate isolated:	.. 78.4 g

Reuse 2

Amt. of m-nitro toluene added:	.. 81.0 g
No. of amp-hrs passed:	.. 112.5 amp-hrs
Temperature to which catholyte was cooled:	.. 20°C
Wt. of m-toluidine sulphate isolated:	.. 60.3 g

Reuse 3

Amt. of m-nitro toluene added:	.. 81.0 g
No. of amp-hrs passed:	.. 112.5 amp-hrs
Temperature to which catholyte was cooled:	.. 20°C
Wt. of m-toluidine sulphate isolated:	.. 110.0 g

Overall

Total wt. of m-nitro toluene	..	404.7 g
Total wt. of m-toluidine estimated as solid	..	244.9 g
Total wt. of m-toluidine in solution	..	36.4 g
Overall yield efficiency:	..	89.1%
Overall current efficiency:	..	71.3%
Energy consumption:	..	11.6 Kwh/kg m-toluidine produced.

WE CLAIM:

1) An improved electrolytic process for the production of m-toluidine from m-nitro toluene in an electrolytic cell having an acid medium as an electrolyte characterised in that m-nitro toluene is electrochemically reduced as a suspension in an electrolyte consisting of sulphuric acid and an admixture of 2-4% of titanium sulphate and 0.05-0.2% of hydrated copper sulphate as an additive, cooling and isolating the m-toluidine sulphate formed and reusing the electrolyte for further reduction.

2) Process as claimed in claim 1 wherein a stationary cathode with a current density of upto 10 A/dm^2 is used.

3) Process as claimed in claim 1 wherein a rotating cathode with a current density of upto 25 A/dm^2 is used.

4) Process as claimed in any one of the preceding claims wherein the electrolyte used consists of 30-40% sulphuric acid and an additive of an admixture of 2-3% titanic sulphate and 0.1% of hydrated copper sulphate.

5) An improved electrolytic process for the production of m-toluidine from m-nitro toluene substantially as herein described and illustrated.

6) An electrolytic cell for carrying out the process as claimed in any of the preceeding claims which comprises a stationary or rotating electrode of copper as cathode, a strip of lead or lead-silver alloy (1% silver) as anode and a ceramic porous pot as a diaphragm, separating the cathode and anode compartment at a temperature between 40-60°C.

7) A cell as claimed in claim 4 wherein the cathode used is a stationary cathode and the current density is upto 10 A/dm^2.

8) A cell as claimed in claim 4 wherein the cathode used is a rotating cathode and the current density is upto 25 A/dm^2.

Dated this 19th day of April, 1980.

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